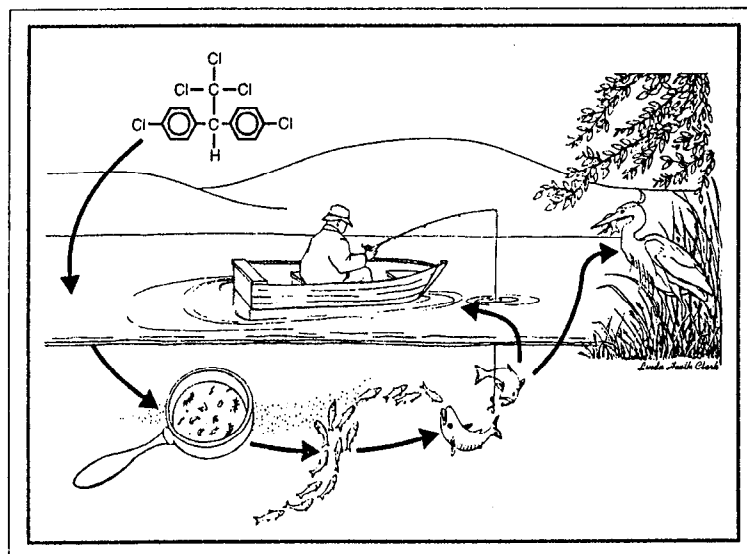


Physico-Chemical Properties and Environmental Fate of Pesticides

By

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ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

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EH 94-03

Preface

The topics discussed in this reference guide are designed to help someone with a basic knowledge of chemistry understand the physico-chemical properties governing the distribution of pesticides in the environment. This guide is meant to be introductory and a general guide. The material is discussed in broad statements without consideration for other details and exceptions. For more in-depth understanding on these topics I suggest that the reader consult the references cited.

This reference guide was written while I worked as a student intern for the Department of Pesticide Regulation under the direction and guidance of Kean S. Goh,

Acknowledgments

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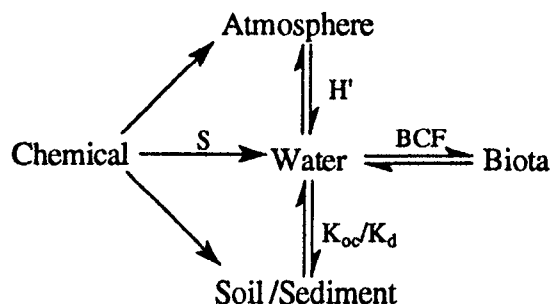
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Introduction: Fate of Pesticides

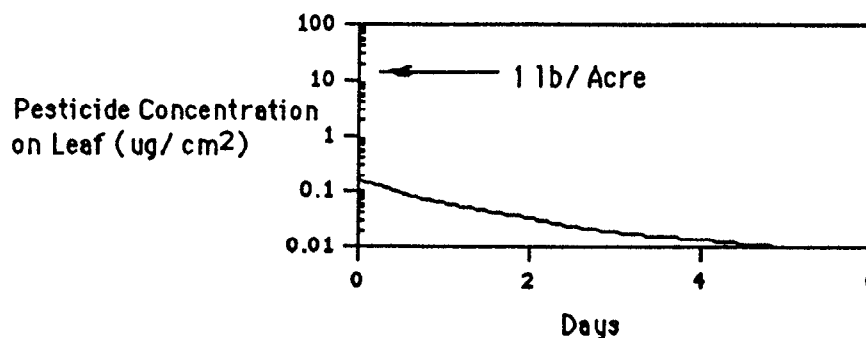


Introduction

When a pesticide is used in the environment, it becomes distributed among four major compartments: water, air, soil, and biota (living organisms). The fraction of the chemical that will move into each compartment is governed by the physico-chemical properties of that chemical. An example is BCF (bioconcentration factor), which is a measure of the amount of pesticide that will accumulate in aquatic organisms. These properties and their relationships to environmental compartments are illustrated in the figure at the top of the page. Most sections start with a figure to help the reader understand how each topic is interrelated.

Overview

When a pesticide is applied to a field, it becomes distributed in the environment. For example, parathion was aerially applied at 1 lb per acre (about 15 mg/cm²). The amount that was detected on the leaves directly after application was little more than 0.1 mg/cm². This means that about 98% didn't reach the leaves. The undetected amount went elsewhere in the environment, being distributed mostly in the soil and air compartments. The following figure shows that over 6 days the amount of parathion in the leaves slowly diminished to a non detectable amount.



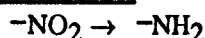
The question is where did the parathion go? Matter cannot be created nor destroyed, so the chemical didn't just disappear. Parathion was being distributed throughout the environment and also becoming mineralized to CO₂, H₂O and phosphates. If the site of pesticide application had been tested for degraded products of parathion, they would have been found in greater abundance as time progressed. Not all pesticides behave alike but this example was used to illustrate how quickly a chemical can be distributed and degraded in the environment.

Pesticides are distributed in the environment by physical processes such as sedimentation, adsorption, and volatilization. They can then be degraded by chemical and/ or biological processes. Chemical processes generally occur in water or the atmosphere and follow one of four reactions: oxidation, reduction, hydrolysis, and photolysis. Biological mechanisms in soil and living organisms utilize oxidation, reduction, hydrolysis and conjugation to degrade chemicals. The process of degradation will largely be governed by the compartment (water, soil, atmosphere, biota) in which the pesticide is distributed, and this distribution is governed by the physical processes already mentioned. The following table shows examples of the different types of reactions that can occur in the degradation process. Reduction, hydrolysis, oxidation, and conjugation will be discussed in their appropriate sections.

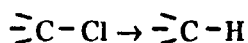
Reduction

Nitro

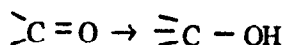
Reaction



Aliphatic Cl

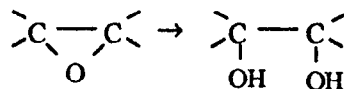


Carbonyl



Hydrolysis

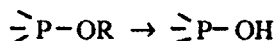
Epoxide



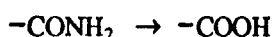
Carboxylic ester



Phosphate ester

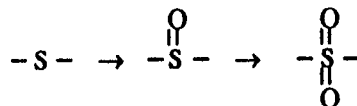


Amide

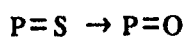


Oxidation

Sulfoxidation



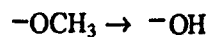
Desulfuration



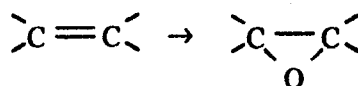
N-dealkylation



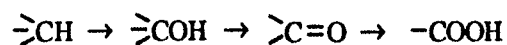
O-dealkylation



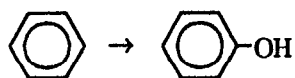
Epoxidation



C-hydroxylation

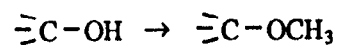


Benzene ring
hydroxylation

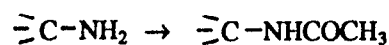


Conjugation

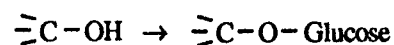
methylation (fungi)



Acetylation (bacteria)

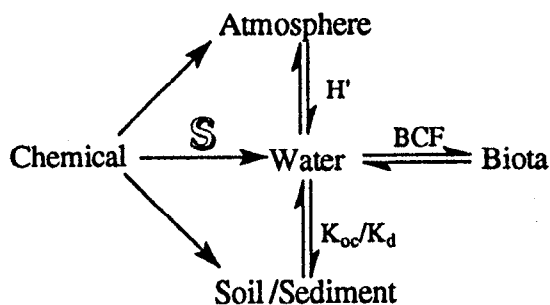


Glucosylation (bacteria)



The following chapters should be read together for a complete overview of the distribution of pesticides in the environment.

Chapter 1: Solubility - S



Introduction

If a chemical's water solubility is known the distribution of that chemical in the environment and possible degradation pathways can be determined. For example, chemicals that have high solubilities will remain in water and tend to not be adsorbed on soil and living organisms.

Definition

Solubility is a measure of the amount of chemical that can dissolve in water. The units of solubility are generally in ppm (parts per - million) which is mg/L (milligrams per liter). It can also be stated in ppb (parts per - billion) which is $\mu\text{g/L}$ (micrograms per liter). The following is an explanation of ppm.

$$1 \text{ part per million} = 1 \text{ ppm} = \frac{1}{1 \text{ million}} = \frac{1 \text{ mg}}{1 \times 10^6 \text{ mg}} = \frac{1 \text{ mg}}{1 \text{ kg}} = \frac{1 \text{ mg}}{1 \text{ L}}$$

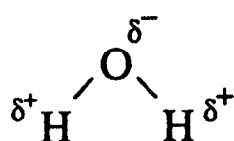
Factors affecting solubility

Polarity

This physical property can be used to understand the underlying basis for how a chemical will be distributed in the environment, whether it will accumulate in soil, water, or living organisms.

Polarity means an unevenness of charge in a molecule.

The alignment of hydrogen and oxygen in a water molecule produces a polar molecule because one end is predominantly negative and the other positive. The following illustration shows a water molecule and the charges on the hydrogen and oxygen atoms.



Direction of the flow of charge.
This flow causes polarization.

Oxygen is a very electronegative atom that attracts electrons in order to increase its stability. Hydrogen is not as electronegative as oxygen so each hydrogen donates part of its electron (electron density) to oxygen. This is represented by the diagram above, δ^+ means that hydrogen has a partial positive charge on it since it has lost some electron density. δ^- on oxygen means that it is gaining electron density so oxygen has a partial negative charge. The degree of the unevenness of charge determines the polarity of a given chemical. Water is polar because of this difference in charge.

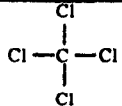

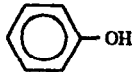
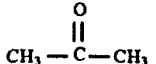
Polarity can be determined from electronegativities and every element has a varying electronegativity as shown on the following table:

H 2.1																	He 0.0
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne 0.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar 0.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 0.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 0.0
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	Rn 0.0
Fr 0.7	Ra 0.9	Ac 1.1															

(Crosby 1993)

Electronegativity represents an elements attractiveness for electrons. The values range from 0 to 4, where 4 is the strongest. If two atoms are bonded together, such as O-H in water, the absolute value of the difference in electronegativity is $3.5 - 2.1 = 1.4$. As the difference gets larger the bond is more polar. If the difference is less than one, the bond is thought to be non-polar. An example is the C-H bond $2.5 - 2.1 = 0.4$, which is non-polar. This simple model can be extrapolated to larger molecules made up of many bonds, where each bond exerts its own polarity. The sum of these polarities gives the

polarity for the entire molecule. Trying to sum up polarities can be difficult so a dipole moment (μ) is used as an approximation for polarity. A dipole moment is a measure of the separation in charge for a molecule, which is much like polarity. The following table shows different solubilities compared to dipole moments for some organic solvents.

Chemical	Chemical Formula	Water Solubility mg/L	Dipole Moment
Carbon tetrachloride		800	0
Benzene		1780	0
Phenol		82000	1.45
Acetone		completely soluble	2.88

(Lyman 1990)

The values show that the tendency is for polar chemicals (high dipole moment) to dissolve in water which is polar and non-polar molecules tend to partition in non-polar environments such as living organisms or soil since these things are made up of molecules comprising C-H bonds which are non-polar. The relationship between dipole moment and solubility is not a strict one, but it is a good estimate.

Hydrogen bonding

This is a term used for a very strong bond that occurs between a molecule containing hydrogen and a more electronegative molecule containing either nitrogen, oxygen or fluorine. This bond can make molecules that have low polarities water soluble because it hydrogen-bonds with the water. The force becomes less important as the molecules become larger.

Molecular size

Molecules of the same polarity but different size will not have the same solubility. As the size increases, the water solubility decreases.

Temperature

Solubility in water is a function of temperature. As the temperature increases most chemicals become more soluble.

pH

As the pH increases, the solubilities of some chemicals will be affected. The ones affected will generally be those that contain acid groups which can change their polarity at different pH.

Symmetry

As a general rule of thumb, the more symmetrical a molecule is, the less soluble it will be in water.

Determination of solubility

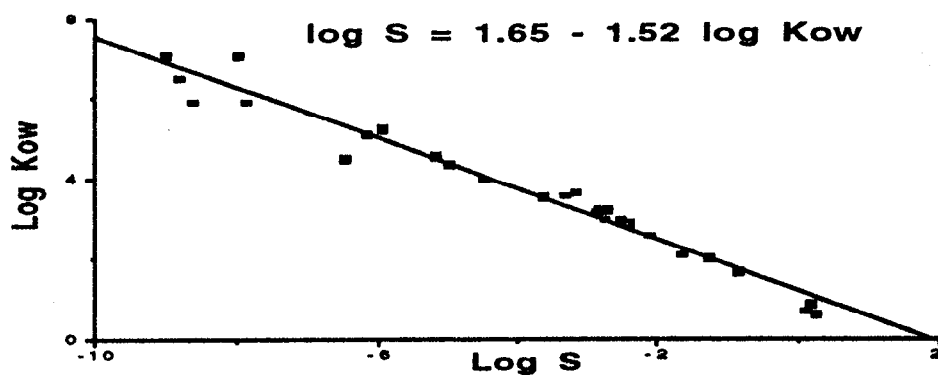
The method for determining water solubility is fairly direct. The chemical is dissolved in water until saturation occurs which is the point at which no more chemical will dissolve. The temperature is kept constant since a small change in temperature can influence the solubility. Excess chemical is removed via filtration and the concentration is measured to determine the solubility of the chemical in water.

Estimation

#	Basis for Method	Required information	Comments
1	Regression equations	K_{ow} (octanol/water partition coefficient)	* Several equations available * Easy to calculate
2	Regression equations	K_{oc} (soil adsorption coefficient)	* Simple calculations * Less accurate
3	Regression equations	BCF(bioconcentration factor)	* Simple calculations * Less accurate

(Lyman 1990)

Methods 1,2 and 3 utilize regression equations to estimate the solubility for a given chemical. The regression equations are derived from graphs where $\log S$ (solubility) is plotted against another variable, such as $\log K_{ow}$ (octanol/water partition coefficient). These graphs are used because there are known relationships between solubility and K_{ow}/K_{oc} (soil adsorption coefficient)/BCF (bioconcentration factor) for these chemicals. A best fit line is plotted through the points and an equation of that line is the regression equation, which can be used to calculate a chemicals solubility value. Following is an example of a regression equation and its corresponding graph.



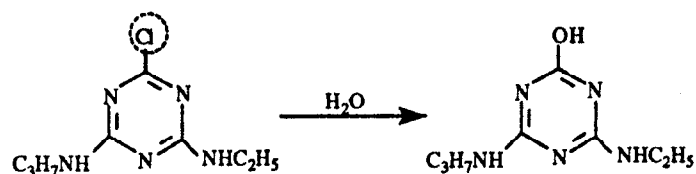
Comparison of Solubility Values

Chemical	Structure	Solubility (ppm)
DDT		0.003
Lindane		10
Atrazine		33
Carbaryl		110
DBCP		1000
Aldicarb		6000
Dicamba		6100
Methyl Bromide	CH_3Br	9200

(Seiber 1991)

Significance in environmental fate

A chemical that is very soluble in water will tend to not accumulate in soil or biota because of its strong polar nature. This suggests that it will degrade via hydrolysis which is the reaction that is favored in water. The following example shows the hydrolysis of atrazine.



A chemical with a high solubility and vapor pressure generally will vaporize and be transported by air. The following table shows how solubility can indicate where a chemical will be distributed. Percentages are shown for distribution in soil sediments, water, and biota. The table shows that chemicals that are not very soluble tend to be adsorbed in soil sediments or biota.

Chemical	Structure	Solubility ppm	Distribution in environment(%)		
			% in Soil Sediment	% in Water	% in Biota
DDT		.003	98.6	1.31	0.081
Chlorpyrifos		0.3	75.3	24.7	0.020
Lindane		10	39.4	60.6	0.011
2,4 D		900	3.16	96.8	0.0003

(Crosby 1993)

Chapter 2: Octanol/Water Partition Coefficient - K_{ow}

Introduction

Partition coefficient is an indicator of the environmental fate of a chemical since it gives a general idea of how a chemical will be distributed in the environment.

Definition

K_{ow} (octanol/water partition coefficient) is defined as the ratio of a chemical's concentration in octanol divided by its concentration in water.

$$K_{ow} = \frac{\text{Concentration in Octanol Phase}}{\text{Concentration in Water Phase}}$$

In this equation the units of concentration cancel so values of K_{ow} are unitless. Values for organic chemicals can be quite large so K_{ow} is generally expressed in 'log K_{ow} ' and the values range from -3 to 7. Low values are easily measured since the chemical stays in water. Log K_{ow} values larger than four must be estimated because they cannot be easily measured. Chemicals with large K_{ow} values are of great concern since they can be adsorbed in soils and living organisms.

Factors influencing Partition Coefficient

Polarity

The more polar a molecule is, the more soluble it will be in water since water is very polar (see Polarity on page 4). This follows the old saying that like dissolves like. Polar molecules will have a low K_{ow} .

General physical factors

A general rule is that K_{ow} will increase as each of these physical properties increases: molecular surface area, boiling point, molar volume, molecular weight, and density (Mallhot 1988).

Determination of Partition Coefficient

Values are measured by adding a chemical to a separatory funnel containing octanol and water. Time is allowed for equilibration and then the concentrations in each fraction are measured. There is variability in accepted values for each chemical because of error introduced in the method such as inconsistent temperature, and other variables. Published K_{ow} values for methyl parathion that are shown below are an example of this variability.

K_{ow}
109.6
977.2
81.3
1659.6

(Lyman 1990)

K_{ow} values are allowed a plus or minus one order of magnitude difference (Lyman 1990).

Estimation

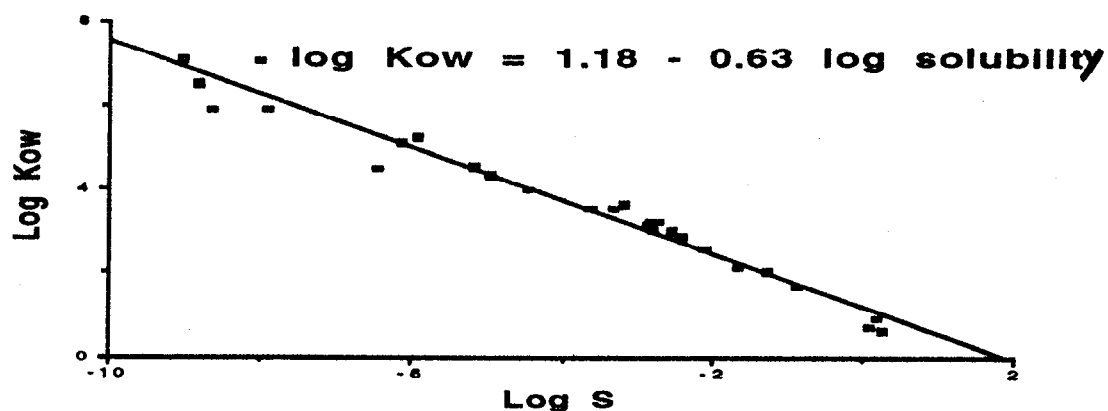
K_{ow} can be estimated by various techniques which are outlined below:

#	Basis for Method	Required information	Comments
1	Regression equations	Solubility	* Easy, rapid calculations * Wide range of applicability * Very accurate
2	Fragment constants and structural factors	Structure(K_{ow} for structurally related compound)	* Fairly accurate * Wide range of applicability * Requires some practice
3	Regression equations	K_{oc} (soil adsorption coefficient)	* Relatively large method error
4	Regression equations	BCF(bioconcentration factor)	* Relatively large method error

(Lyman 1990)

Methods

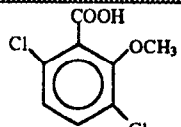
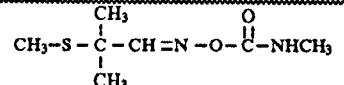
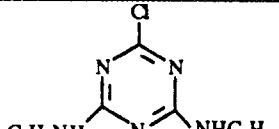
Methods 1, 3, and 4 use regression equations to estimate K_{ow} for a given chemical. Regression equations are derived from graphs where $\log K_{ow}$ is plotted against another variable, such as solubility (S). These graphs are used because there are known relationships between partition coefficient (K_{ow})/ soil adsorption coefficient (K_{oc})/ bioconcentration factor (BCF)/ and Solubility (S) for these chemicals. A best fit line is obtained from the points on the graph and the equation of that line is the regression equation. Now this equation can be used to calculate a K_{ow} value for a chemical by inserting its solubility value into the equation. The following is an example of a regression equation and its corresponding graph.

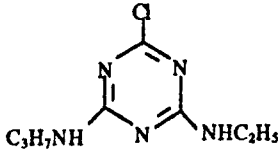
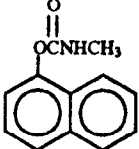
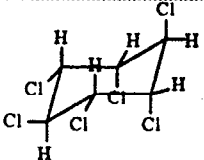
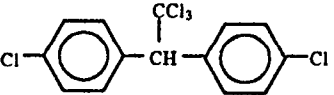


Method 2 requires only a knowledge of the chemical structure. Each fragment of a molecule has a different constant that can be looked up in a table. The constants are summed together to obtain a log K_{ow} value.

Comparison of Partition Coefficient Values

K_{ow} values are important in that they can be used to estimate many chemical properties such as solubility and BCF (bioconcentration factor) since they are proportional to K_{ow} . The following table shows K_{ow} values along with water solubility and BCF values. They are shown together so that you can get a feel for how they are related. In general, a high K_{ow} corresponds to a low water solubility and a high BCF.

Chemical	Structure	log K_{ow}	Water Solubility (ppm)	BCF
Methyl Bromide	<chem>CH3Br</chem>	-	9200	-
Dicamba		.48	6100	-
Aldicarb		.7	6000	2
Simazine		1.90	5	100

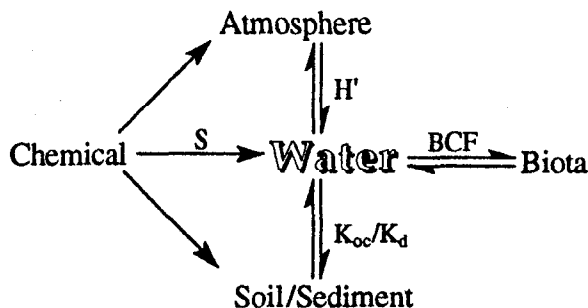
Chemical	Structure	log K _{OW}	Solubility (ppm)	BCF
Atrazine		2.30	33	110
Carbaryl		2.50	110	46
Lindane		3.7	10	169
DDT		6.11	0.003	29700

(Seiber 1991)

Environmental significance

In general, a large K_{OW} value means that a chemical tends to be in an organic (non-polar) environment and not in water (polar). This means that it will have a low water solubility. Most pesticides are less polar than water so they tend to accumulate in soil or living organisms which contain organic matter. So one can see that K_{OW} values give an overall estimate as to where a chemical will be distributed in the environment.

Chapter 3: Hydrolysis

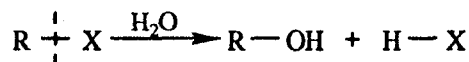


Introduction

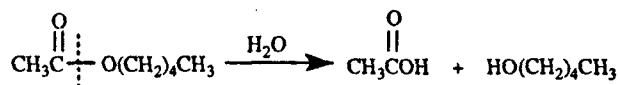
Hydrolysis is an important reaction that takes place in water for pesticide degradation. A pesticide reacts with water to form degradation products that can be distributed in the environment.

Definition

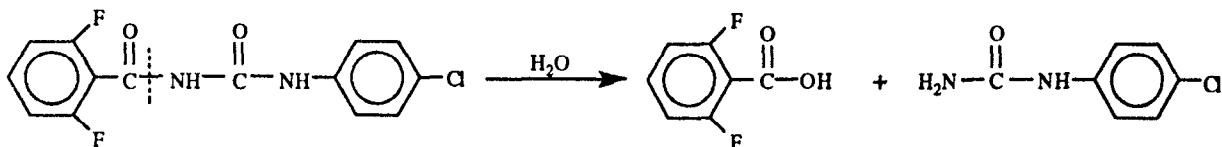
Hydrolysis means that a chemical has reacted with water to form a new product. Pesticide hydrolysis rates are generally described in half lives (see appendix) which is the amount of time it takes for half of an amount of a chemical to be hydrolyzed. The following is a general reaction format for hydrolysis where the molecule R-X reacts with water to form R-OH and H-X.



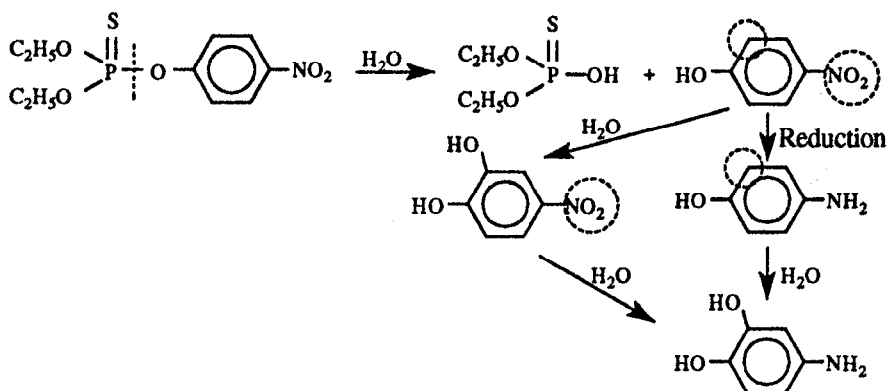
If $R=O(CH_2)_4CH_3$ and $X=CH_3C(=O)-$, the hydrolysis reaction is:



The bond between R and X breaks and OH^- from water forms a new bond with R. The following illustration is the hydrolysis reaction for diflubenzuron.



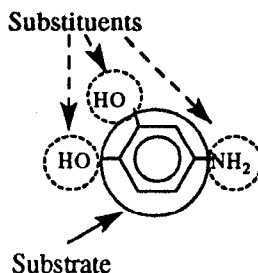
Hydrolysis reactions are not always just one step, there can be several steps and different pathways that hydrolysis can follow. The following illustration of the hydrolysis of parathion illustrates this principle.



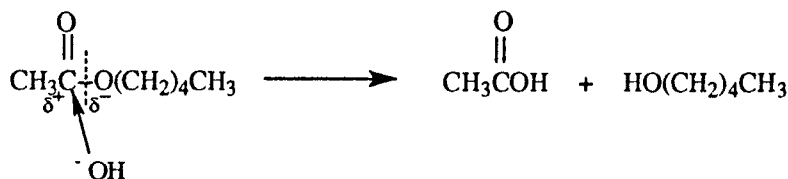
Factors Influencing Hydrolysis

Substituents

A chemical's reactivity is the most important factor determining whether hydrolysis will occur. This reactivity is largely determined by the substituents that are bound to the chemical. Substituents are atoms or groups of atoms bonded to the substrate (main body of chemical). The following illustration shows substituents and substrates.



Some substituents are readily displaced from the substrate by hydrolysis reactions since the products formed are very stable in water. There are other substituents that pull electron density away from the substrate, making a partially positive center that readily accepts hydrolysis. This is shown in the following example.

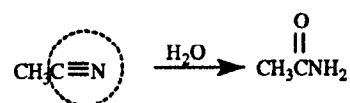


Temperature

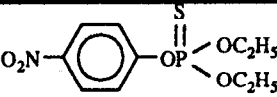
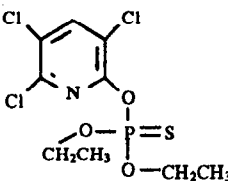
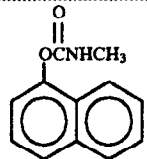
As the temperature increases the molecules in solution have more energy, causing them to move and react faster. This causes hydrolysis reactions to occur at a faster rate.

pH

Some hydrolysis reactions work better in slightly basic or acidic environments. The previously shown mechanism needs a slightly basic solution to start, because it is the OH^- that is attracted to the carboxyl center (carbon double bonded to the oxygen). The next reaction needs a slightly acidic solution so the nitrogen can be doubly protonated (add two hydrogens to nitrogen).



The following table shows how a difference in pH can affect hydrolysis half life ($t_{1/2}$).

Chemical	Structure	pH	$t_{1/2}$ (days) (at 25°C)
Parathion		5	133
		7	247
		9	102
Chlorpyrifos		5	72.8
		7	72.1
		9	29.4
Carbaryl		5	1230
		7	11.6
		9	0.134

(Crosby 1993)

Determination of Hydrolysis Half Life

Hydrolysis half life ($t_{1/2}$) is determined by adding a known amount of chemical into a solution and then measuring the amount of the original chemical present at various time intervals. Then a graph of the natural log of chemical present vs time is plotted. The slope of the line will equal the value K_T (Hydrolysis rate constant). $t_{1/2}$ can then be determined by using K_T in the equation:

$$t_{1/2} = 0.693/K_T.$$

Hydrolysis is very temperature sensitive because an increase of 1° C can increase the rate by 10% and a difference of 10° C can affect the rate by as much as a factor of 2.5 (Lyman 1990).

Estimation

The rate of hydrolysis can be estimated by the two methods shown in the following table. The rate of hydrolysis in acidic solution differs from hydrolysis in basic solution, so different equations must be used for each. The rate is estimated by using complex correlations between the reactivity of the substituent and its replacement by water. These equations take into account the strength of the bonds, liquid temperature, and the speed of reaction. The following table shows which correlation equations are used to calculate the hydrolysis rate constant at different pH values.

Estimated variable	Method	Chemical classes covered
K_H	Hammett Correlation	Ring-substituted benzamides; ethyl benzoates
K_H	Taft Correlation	Ortho-substituted benzamides
K_o	Hammett Correlation	Benzyl halides; dimethyl benzyl halides; benzyl tosylates
K_{OH}	Hammett Correlation	Benzene ring substituted compounds
K_{OH}	Taft Correlation	Dialkyl phthalate esters

K_H = Rate constant for acid catalyzed hydrolysis ($M^{-1} s^{-1}$)

K_o = Rate constant for neutral hydrolysis (s^{-1})

K_{OH} = Rate constant for base catalyzed hydrolysis ($M^{-1} s^{-1}$)
(Lyman 1990)

These constants from the table are then used in the equation:

$$K_T = (K_H * 10^{-pH}) + K_o + (K_{OH} * 10^{pH-14})$$

K_T is the rate of the overall hydrolysis reaction. The hydrolysis half life ($t_{1/2}$) can then be calculated by using K_T in the following equation:

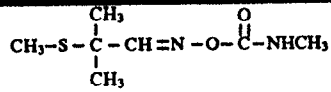
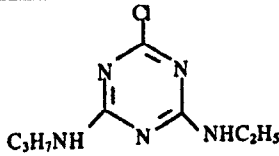
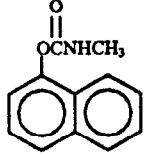
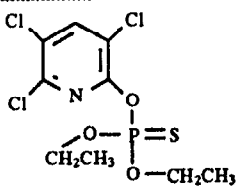
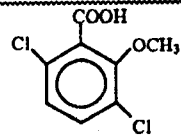
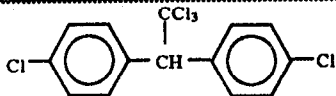
$$t_{1/2} = 0.693/K_T$$

This method is accurate but is unable to take into account changes in temperature and effects caused by other chemicals which vary in the environment.

Comparison of Hydrolysis Half-Lives

The half life of a chemical in solution can be easily influenced by changes in temperature, particulates in solution, and other chemicals.

Each chemical is assigned a range of values for its half life because of variability in hydrolysis rates under different environmental conditions.

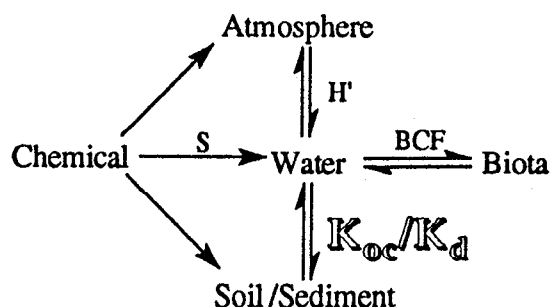
Chemical	Structure	t _{1/2} (days)
Aldicarb		42 - 180
Atrazine		42 - 180
Carbaryl		<14
Chlorpyrifos		<14
Dicamba		14 - 45
DDT		>180

(McEwen 1979)

Environmental Significance

Hydrolysis half life values will help one to estimate how long a chemical will persist in an aqueous environment. If the chemical resists hydrolysis then it may degrade via some other pathway such as microbial metabolism.

Chapter 4: Soil Adsorption Coefficient - K_{oc}/K_d



Introduction

Adsorption of pesticides on soils or sediments is a major factor in the transportation and eventual degradation of chemicals. Most pesticides are non-polar and hydrophobic, which means that they are not very soluble in water. Water solubilizes polar chemicals because it can bond with them more easily. Chemicals that are non-polar tend to be pushed out of water and onto soils which contain non-polar carbon material. Soils vary in the amount of organic carbon content, which is mainly what determines the amount of pesticide adsorbed. K_d is called the sorption coefficient and it measures the amount of chemical adsorbed onto soil per amount of water. Values for K_d vary greatly because the organic content of soil is not considered in the equation. The preferred value for determining a soil's ability to adsorb is K_{oc} , since it considers the organic content of the soil.

Definition

$$K_d = \frac{\text{Concentration of chemical in soil}}{\text{Concentration of chemical in water}}$$

$$K_{oc} = \frac{K_d \times 100}{\% \text{ organic carbon}}$$

Factors influencing Soil Adsorption Coefficient

Organic Carbon Content

The amount of carbon present in soil is probably the greatest factor influencing the amount of chemical adsorbed. This is because organic matter is non-polar and has a relatively light negative charge. Most pesticides are non-polar and will be attracted to the lightly charged surface. As the organic content of soil increases so does the amount adsorbed. The following table shows how values of K_d vary as the organic content in soil is changed.

Chemical	K_d	Organic matter(%)
EDB	21 \leftrightarrow 93	0.5 \leftrightarrow 21.7
Napropamide	110 \leftrightarrow 1223	0.1 \leftrightarrow 2.4
Parathion	182 \leftrightarrow 9200	0.2 \leftrightarrow 6.1
Lindane	427 \leftrightarrow 1502	1.2 \leftrightarrow 20.5
Chlorpyrifos	1255 \leftrightarrow 20400	1.2 \leftrightarrow 6.6
Dieldrin	2302 \leftrightarrow 7122	0.7 \leftrightarrow 28.9
DDT	76300 \leftrightarrow 257040	1.6 \leftrightarrow 3.9

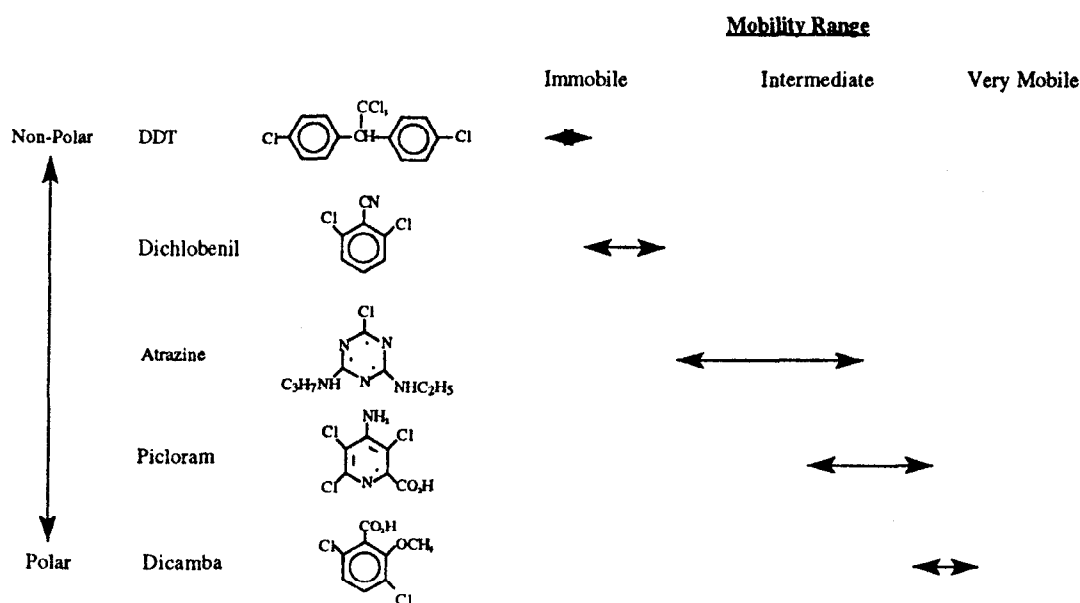
(Mingelgrin 1983)

The difference in percent organic content can make an order of magnitude difference in the value of K_{oc} . For this reason, K_{oc} is used instead of K_d for soil adsorption because it takes into account the organic content.

Polarity

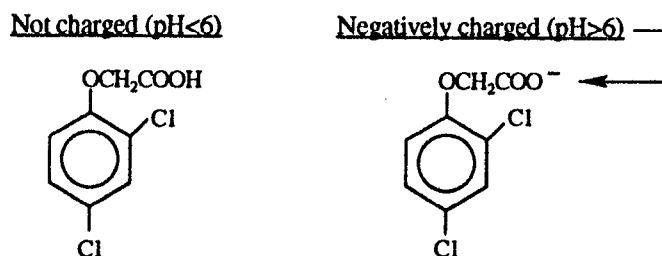
Polarity (see polarity on page 4) greatly determines whether the chemical will partition into the soil. A polar pesticide will be very water soluble and tend not to be adsorbed onto soil. If the pesticide is non-polar it will tend to leave water and be adsorbed onto soil.

Once adsorbed, non-polar molecules will more strongly bind to soils than polar ones, so polar molecules will be more mobile in soil. This process occurs when water is present because the chemical is able to dissolve in water and move through soil. The chemical moves by dissolving and being deposited on another portion of soil and the process continues. This movement is what allows pesticides to reach ground water. This is shown in the following illustration.



pH

Weak acids and bases are generally the only ones affected by pH. For example, 2,4-D is in a nonionic form at pH less than 6 and it is in an anionic (negative) form at pH greater than 6. The following two structures show these forms of 2,4-D.



Soil has a slight negative charge (acidic) so it tends to absorb positively charged to noncharged chemicals. 2,4-D will tend to be absorbed at soil pH less than 6 but it will not be absorbed as much if 2,4-D is in its charged form because the two negative charges (soil and chemical) will repel each other. Pesticides that are not ionizable are generally not affected by pH.

Salinity

An increase in the amount of salts present in water will generally decrease the amount of chemicals adsorbed that are in the cationic (positive) form. This is due to the competition for bonding sites on the soil.

Organic matter in solution

Organic matter can be dissolved or suspended in water. Non-polar chemicals can be adsorbed by this organic matter in water which can then settle to the floor or be transported away.

Determination of K_{oc} and K_d

Soil sorption coefficient can be determined by gently shaking a aqueous sample of soil that contains a chemical. The suspension is then centrifuged and analyzed. The adsorption is determined by calculating the difference between the amount of chemical added and the amount found in solution.

Estimation

There are also a variety of linear regression equations that can estimate K_{oc} values. These equations use the relationships that K_{oc} has with solubility, K_{ow} (octanol/water partition coefficient), and BCF (bioconcentration factor). Generally, the correlation with solubility is the best since the chemical is being adsorbed onto the soil from water. These equations are useful but they are not always correct

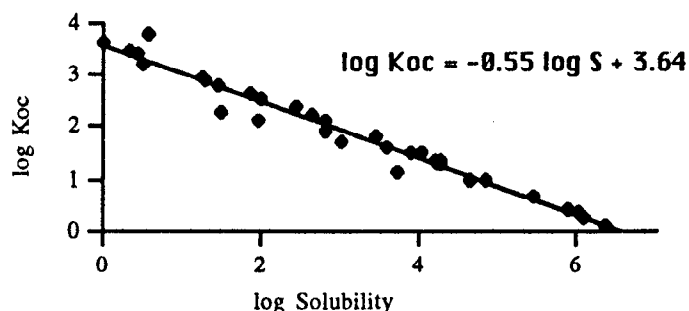
since there are some chemicals that are very soluble in water and tend to be adsorbed in soils as well.

Estimation methods

#	Method	r ²	Chemical Classes Represented
1	$\log K_{oc} = -0.55 \log S + 3.64$.71	* Most pesticides
2	$\log K_{oc} = -1.54 \log S + 0.44$.94	* Aromatic hydrocarbons * Polynuclear aromatic hydrocarbons
3	$\log K_{oc} = -0.56 \log S + 4.28$.99	* Chlorinated hydrocarbons
4	$\log K_{oc} = 0.54 \log K_{ow} + 1.38$.74	* Most pesticides
5	$\log K_{oc} = 1.0 \log K_{ow} - 0.21$	1.00	* Aromatic hydrocarbons * Polynuclear aromatic hydrocarbons
6	$\log K_{oc} = 0.68 \log BCF + 1.96$.76	* Most pesticides
7	HPLC retention times	-	* Most pesticides * Very accurate

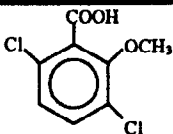
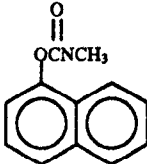
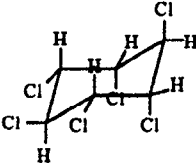
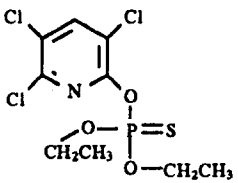
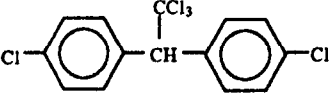
(Mingelgrin 1983) & (Lyman 1990)

Methods 1, 2, 3, 4, 5 and 6 use regression equations to estimate the soil adsorption coefficient for a given chemical. The regression equations are derived from graphs where $\log K_{oc}$ is plotted against another variable, such as Solubility (see solubility page 4). A best fit line is obtained from the points and the equation of that line is the regression equation. This equation can be used to calculate a K_{oc} value for a chemical given its solubility by inserting the log solubility value into the equation. Below is an example of a regression equation and its corresponding graph.



For method 7 the chemical is run on an HPLC (High Performance Liquid Chromatography), which is an instrument that separates chemicals according to their polarity (see polarity on page 4). The retention times for the chemical are compared with known values for other chemicals to determine the K_{oc} value. This method is generally quick and easy to perform.

Comparison of Soil Adsorption Values

Chemical	Chemical Structure	K _{oc}	Water Solubility (ppm)
Dicamba		0.4	4500
Carbaryl		230	40
Lindane		911	0.150
Chlorpyrifos		13600	0.3
DDT		238000	0.0017

(Kenaga 1980)

Environmental Significance

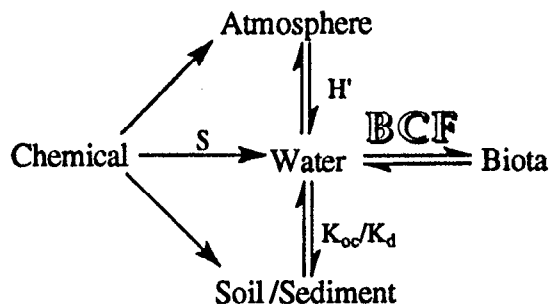
There are two major ways that pesticides can reach surface and ground waters: runoff and leaching. Runoff will occur if the chemical does not adsorb onto soil. Leaching occurs when the chemical is weakly adsorbed by soil and can easily move through the soil. Weak acid pesticides are bound weakly to soil so they can easily move downward to ground waters. Below is listed where a chemical is likely to end up depending on its K_{oc} value and its persistence (half life) in the environment.

K _{oc}	Half-life	Pathway of loss	Has potential for contaminating
small	long	leaching	ground water
small	short	leaching	ground water ^a
large	long	runoff	surface water
large	short	runoff	surface water ^a

^aOnly if heavy rains or irrigation occur soon after pesticide application

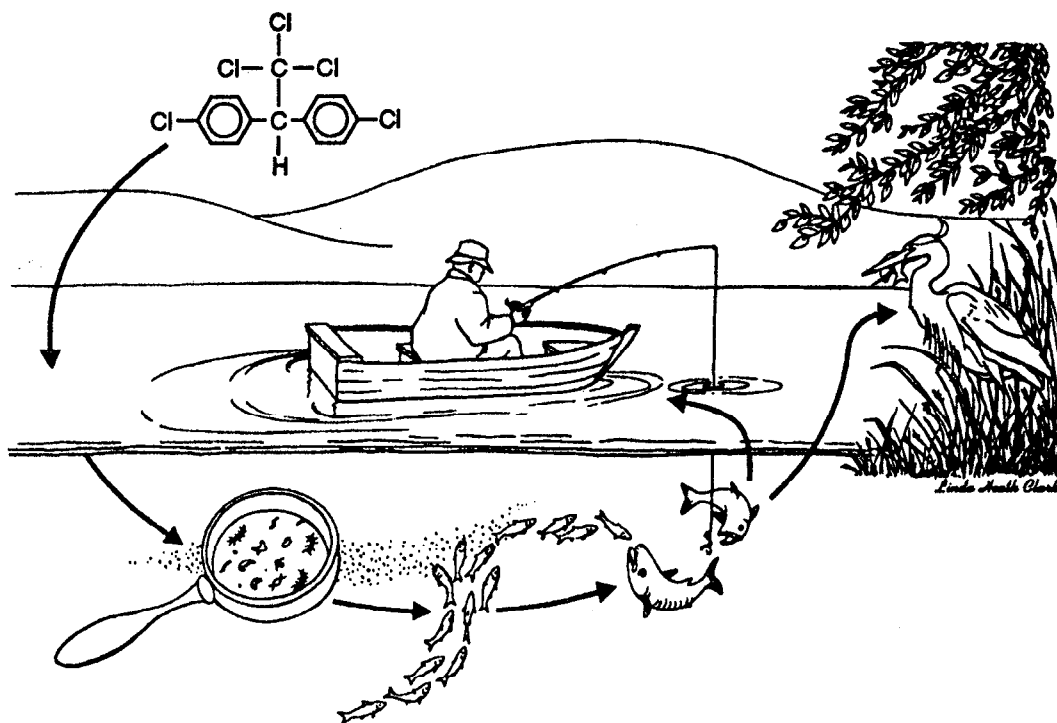
(Rao 1983)

Chapter 5: Bioconcentration Factor - BCF



Introduction

Bioconcentration factor (BCF) is an indicator of how much a chemical will accumulate in living organisms such as fish. Chemicals that have high BCF values are generally no longer used because of possible hazards to living organisms. Once absorbed into an organism, chemicals can move through the food chain as the following illustration shows with DDT.



DDT moves from one organism to another as it is ingested by the next animal in the food chain. The increase in concentration of a chemical as it moves through a food chain is called biomagnification or bioaccumulation. Bioconcentration (BCF) is different from biomagnification in that it is a measure of the absorption of a chemical from an aqueous environment by a single organism.

Definition

BCF is the accumulation of a chemical in living organisms (biota) compared to the concentration in water.

$$\text{BCF} = \frac{\text{Concentration in Biota}}{\text{Concentration in Water}}$$

BCF values are unitless and generally range from one to a million. Bioconcentration is based on the law of equilibrium. For example, if a fish exposed to atrazine has a BCF of 110, the chemical would be absorbed according to the relation:

$$\text{BCF} = \frac{\text{Concentration in fish}}{\text{Concentration in Water}} = 110$$

The ratio of the concentration in fish over the concentration in water equals 110. To reach this the fish will absorb atrazine until the ratio equals 110. So if the concentration of atrazine in water is high, the fish will absorb large amounts to attain the BCF ratio. Likewise, if the concentration in water is low the fish will absorb little. Once equilibrium is reached, the fish will not absorb more of the chemical. Also, if a fish which has some chemicals in it is put into clean water then the fish will release the chemical into the water to attain the ratio (equilibrium). The process of the chemical being released is called depuration.

Factors that influence Bioconcentration Factor:

Polarity:

Polar molecules are soluble in water (polar) and not very soluble in tissues (non-polar). Polar chemicals tend not to bioconcentrate in biota because of this low solubility, whereas non-polar chemicals will accumulate in fatty tissues.(see polarity on page 4).

Solubility

If a chemical is very soluble in water it will tend to stay in water and not accumulate in biota, whereas non-water soluble chemicals are more non-polar and tend to be more likely to accumulate.

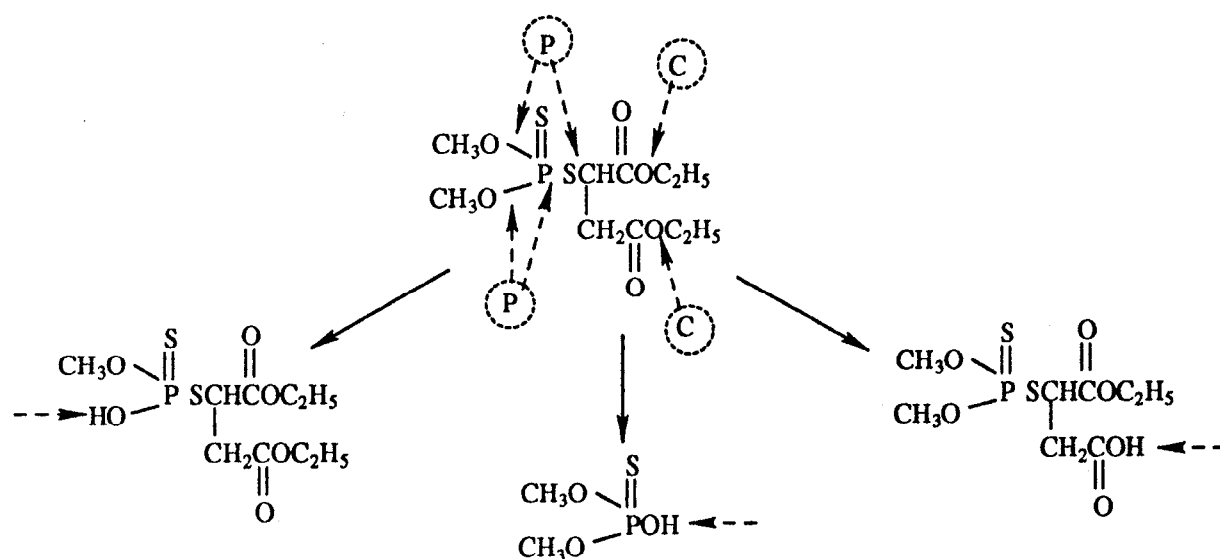
Lipid content

Every living organism has a different lipid content so each will absorb different amounts of a chemical accordingly. If the lipid content is high, the organism will tend to absorb more.

Metabolism

When an animal absorbs a chemical, the biological system of that animal has mechanisms for getting the chemical out of the system. This is done by changing part of the chemical in order to make it water soluble so that it can be expelled through the urine. This process of altering part of a chemical is called metabolism and can take many steps.

The following illustration shows possible metabolic pathways for malathion. The process that occurs depends on the enzymes present in the organism. Circled P stands for degradation by the enzyme phosphatase and circled C stands for the enzyme carboxyesterases. Possible metabolites formed by these two enzymes are also shown below.



Some of the products that are created are expelled when they become water soluble. Sometimes the organism is only able to metabolize the chemical to a certain point because it lacks the enzyme to complete the reaction that will make it water soluble. When this happens the chemical accumulates in fish, just like the parent chemical does.

Earlier it was mentioned that a fish will accumulate a chemical until it reaches its BCF. If the parent chemical is being metabolized, reducing the concentration of the primary chemical, the fish will continue to adsorb more chemical in order to reach equilibrium.

Habitat

The way in which BCF is calculated assumes that the concentration is constant everywhere and that a fish is exposed to the same amount all of the time. In real life this is not true. Concentrations vary in water so a fish will be exposed differently as it swims

around. Also, there are many chemicals present in water at any given time and BCF does not indicate how different chemicals will affect each other during absorption. They could have either a positive or negative effect. In addition, seasonal variations in temperature, salinity, and dissolved oxygen can affect BCF values as well.

Determination of Bioconcentration Factor:

To determine the BCF of organisms, such as fish or mussels, they are placed in a chamber where they are exposed to a known amount of chemical until equilibrium is established. At this time some of the organisms are removed and tested for the amount of chemical absorbed in the tissue. Measurements are also taken of the amount of chemical left remaining in the water. The rest of the living organisms are then put into fresh water where they will release the chemical back into the water, which is called depuration. The amount released is measured as well. These measurements are used to calculate the BCF value.

Estimation

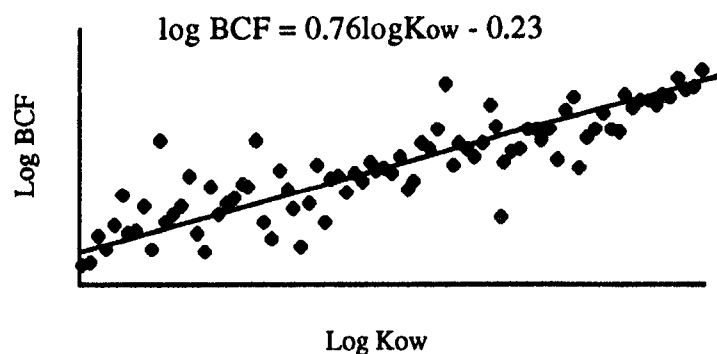
BCF can also be estimated by using relationships it has with other chemical distribution variables such as K_{ow} (octanol/water partition coefficient) and solubility. These relationships are shown below.

#	Equation	r^2	Species used	Number of chemicals used to generate equation
1	$\log BCF = 0.76 \log K_{ow} - 0.23$	0.823	* Fathead minnow * Bluegill sunfish * Rainbow trout * Mosquitofish	82
2	$\log BCF = 2.791 - 0.564 \log S$	0.49	* Brook Trout * Fathead minnow * Bluegill sunfish * Rainbow trout * Carp	36
3	$\log BCF = 0.542 \log K_{ow} + 0.124$	0.899	* Rainbow trout	8

(Lyman 1990)

Methods 1, 2, and 3 use regression equations to estimate log BCF. Regression equations are derived from graphs where log BCF is plotted against another variable, such as K_{ow} . A best fit line is plotted through the points and an equation of that line is the

regression equation, which can be used to calculate a chemicals BCF value. The following is an example of a regression equation for method one and its corresponding graph.



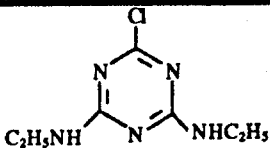
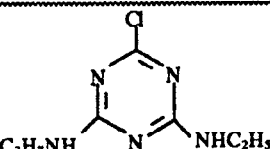
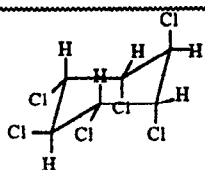
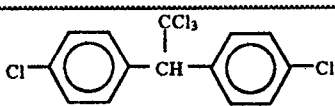
The graph shows that the equation of the line does not perfectly represent each individual value since not all values lie on the line. This error occurs because the equations shown in the graph are generated by using different chemicals and fish species which can introduce two possible errors:

- 1) Every chemical is absorbed in different amounts according to their tendency to partition into lipid material.
- 2) Different species of fish have different lipid content levels so the absorption values will vary.

The error in calculation increases as more chemicals and fish species are used. This indicates that log BCF values obtained from equations 1 and 2 will not give as accurate values as equation 3, since equation 3 uses only one species of fish. Regression equations should be used only when there is not sufficient data to determine the actual BCF value.

Comparison of BCF Values

Chemical	Structure	BCF
Aldicarb	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{S}-\text{C}-\text{CH}=\text{N}-\text{O}-\text{C}(=\text{O})-\text{NHCH}_3 \\ \\ \text{CH}_3 \end{array}$	2
DBCP	$\begin{array}{c} \text{Br} \\ \\ \text{BrCH}_2-\text{CH}-\text{CH}_2\text{Cl} \end{array}$	13
Carbaryl	$\begin{array}{c} \text{O} \\ \\ \text{OCNHCH}_3 \\ \\ \text{C}_{10}\text{H}_7 \end{array}$	46

Chemical	Structure	BCF
Simazine		100
Atrazine		110
Lindane		169
DDT		29700

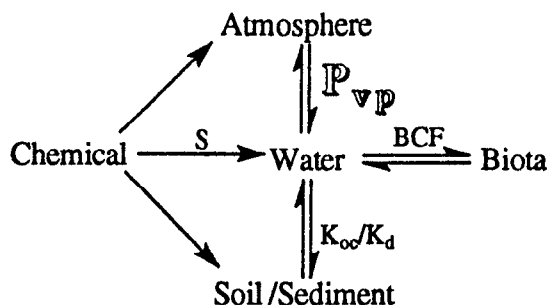
(Seiber 1991)

Environmental Significance

BCF can be an indicator of a chemical's tendency to accumulate in the food chain. Whether they are harmful to living organisms is another story. The main purpose for metabolism is not to detoxify, but to make the chemical more polar so that the chemical will be more water soluble and then be excreted in the urine.

BCF is also a good indicator of where a chemical will be distributed. If BCF is high, the chemical will generally have a low water solubility, a large K_{ow} (octanol/water partition coefficient), and a large K_{oc} (soil adsorption coefficient).

Chapter 6: Vapor Pressure - P_{vp}



Introduction

The three chapters entitled Henry's law constant, vapor pressure, and volatilization are all interrelated in that they deal with how chemicals are transported from a surface into the atmosphere. To obtain a full understanding of this transport process, all three chapters should be read.

Pesticides can contaminate soil, water, air, and biota. Vapor pressure is often used as an indicator of the rate at which a chemical will evaporate. Another feature of vapor pressure is that it will indicate whether a chemical will stay in one area or volatilize and disperse over a large area.

P_{vp} (vapor pressure) is a measure of the pressure that a chemical in air exerts on the surface below. P_{vp} is an integral part in calculating the volatility and Henry's Law constant for a chemical.

Definition

Vapor Pressure is defined as the pressure that a chemical in the gas phase exerts over a surface. This surface can be water or dry soil. At room temperature, P_{vp} values can range from 10^{-5} to 300 mm of Hg (mercury).

Vapor pressure units are generally expressed in three ways: mm Hg (millimeters of mercury), Pa (pascals), atm (atmospheres). The unit *mm of Hg* is a measure of the pressure exerted by a gas on a mercury surface which pushes the mercury level up so many mm (millimeters). The atmospheric pressure on an average day is 760 mm Hg. One *atm* is defined as the pressure exerted by a column of mercury 760 mm high at 0°C. If the pressure is 0.95 atm, then it is said that the pressure is 95% of that exerted by a mercury column 760 mm Hg high. Pascals (Pa) is the preferred unit for pressure and is generally in the form MPa (Mega-Pascals). The relationship between the three units are:

$$1 \text{ atm} = 760 \text{ mm Hg} = 101325 \text{ Pa} = 0.1 \text{ MPa}$$

$$1 \text{ MPa} = 10^6 \text{ Pa}$$

Factors Influencing Vapor Pressure

Factors influencing vapor pressure will be discussed in the chapter on volatilization.

Determination of Vapor Pressure

There are several methods in current use that estimate the vapor pressure of a given chemical. However, most do not give reliable values at low vapor pressures (<1 mm Hg), which are the values that we are interested in for certain environmental problems.

Estimation

One or two methods are relatively reliable for estimating low vapor pressures. These methods rely upon a chemical's physical properties, such as the normal boiling point, polarity, and the heat of vaporization. The equations will not be outlined here (see Lyman 1990). The methods are as follows.

	Method I		Method II		
Basis for calculation	Antoine equation		Modified Watson correlation		
Chemical physical state	Liquid & gas		Liquid & solid		
Range of P_{vp} (mm of Hg)	10^{-3} to 760		10^{-7} to 760		
P_{vp} range calculated	10-760	10^{-3} -10	10-760	10^{-3} -10	10^{-7} - 10^{-3}
Method error (%)	2.7%	86.3%	2.5%	38.7%	46.9%

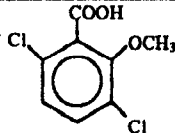
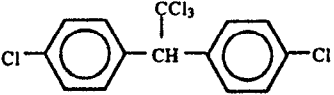
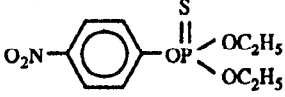
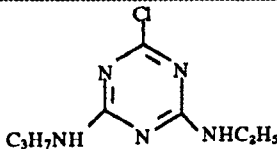
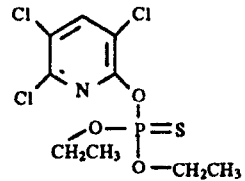
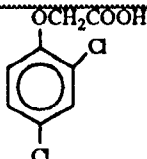
(Lyman 1990)

The table shows that as the calculated values of P_{vp} get smaller more error is found in the result. The error is generally no more than one order of magnitude difference from the actual value, however, sometimes the result may be a poor approximation so a value judgment must be made as to whether the approximation is acceptable. The following table shows some calculated and experimental values for three pesticides.

Chemical	Experimental P_{vp} (mm Hg)	Calculated P_{vp} (mm Hg)	
		Method I	Method II
Dicamba	2×10^{-5}	2×10^{-4}	2×10^{-5}
Aldrin	6×10^{-6}	4×10^{-5}	8×10^{-7}
Endrin	2×10^{-7}	7×10^{-5}	3×10^{-7}

(Lyman 1990)

Comparison of Various Vapor Pressures

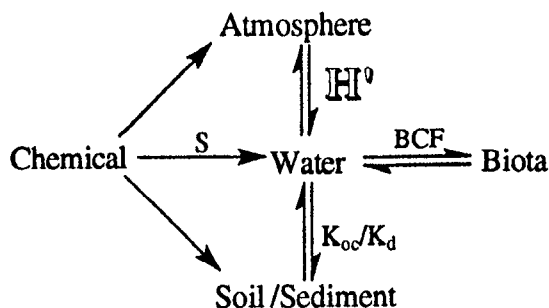
Chemical	Structure	P _{VP} (Pa)
Dicamba		0.00012
DDT		0.00015
Parathion		0.00060
Atrazine		0.0014
Chlorpyrifos		0.0025
2,4-D		27.78

(Suntio 1988)

Environmental Significance

Pesticides with high vapor pressures may become environmental problems because they can volatilize and disperse over a large area. Chemicals with a high vapor pressure need to be handled in such a way so that the vapors do not escape into the atmosphere. A chemical with a low vapor pressure does not move into air so there is a potential for accumulation in water if it is water soluble. If it is not water soluble the chemical may accumulate in soil or biota.

Chapter 7: Henry's Law Constant - H'



Introduction

The three chapters entitled Henry's law constant, vapor pressure, and volatilization are all interrelated in that they deal with how chemicals transport from a surface into the atmosphere. To obtain a full understanding of this transportation process, all three chapters should be read.

Henry's law constant (HLC) is a measure of the concentration of a chemical in air over its concentration in water. A pesticide with a high HLC will volatilize from water into air and be distributed over a large area. Chemicals with a low HLC tend to persist in water and may be adsorbed onto soil. The HLC value is an integral part in calculating the volatility of a chemical. The chapter on volatility will show how this is done.

Definition

Henry's Law constant for a chemical is generally expressed in one of two ways:

$$H' = \frac{\text{concentration in gas phase}}{\text{concentration in liquid phase}}$$

$$H = \frac{\text{liquid vapor pressure}}{\text{chemical solubility}}$$

The first quantity, represented by H' , is dimensionless since the units for concentrations cancel out. Notice that this HLC variable has a hyphen after it to help distinguish it from the second HLC value. The second quantity, represented by H , is usually in units of Pa-m³/mol or atm-m³/mol. These units for H are used because a chemical's vapor pressure (Pa-pascals) and solubility (m³/mol) are used to determine the value.

Factors Influencing Henry's Law Constant

Factors influencing HLC will be discussed in the chapter on volatilization.

Determination of Henry's Law Constant

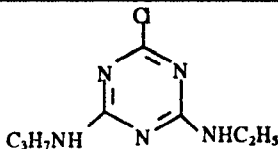
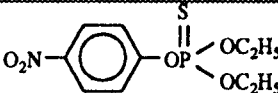
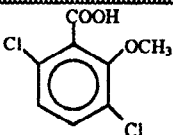
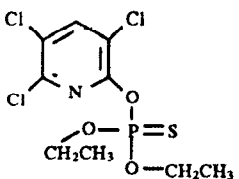
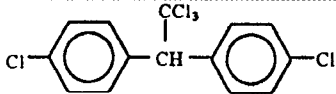
The HLC of a chemical can be measured by using a controlled ecosystem where the environmental conditions (temperature, wind, etc.) are constant. A known amount of chemical is placed in water, and air is passed over the surface. The water concentration is measured over time. The amount of chemical lost can be used to determine the chemical's air concentration and HLC. There are problems with this technique since systems in nature are not constant. There are fluctuations in temperature, wind, and other chemicals in the water which could influence the HLC. The values obtained from this process are just estimates of a chemical's HLC. As HLC becomes smaller (less goes into the air), the values obtained are less accurate because of the difficulty in measuring such a small amount transported into the air.

Estimation

Henry's Law constants can be estimated by using the following equation where P = vapor pressure, M = molecular mass, T = temperature and S = Solubility.

$$H' = \frac{16.04 \cdot P \cdot M}{T \cdot S}$$

Comparison of Henry's Law Constants

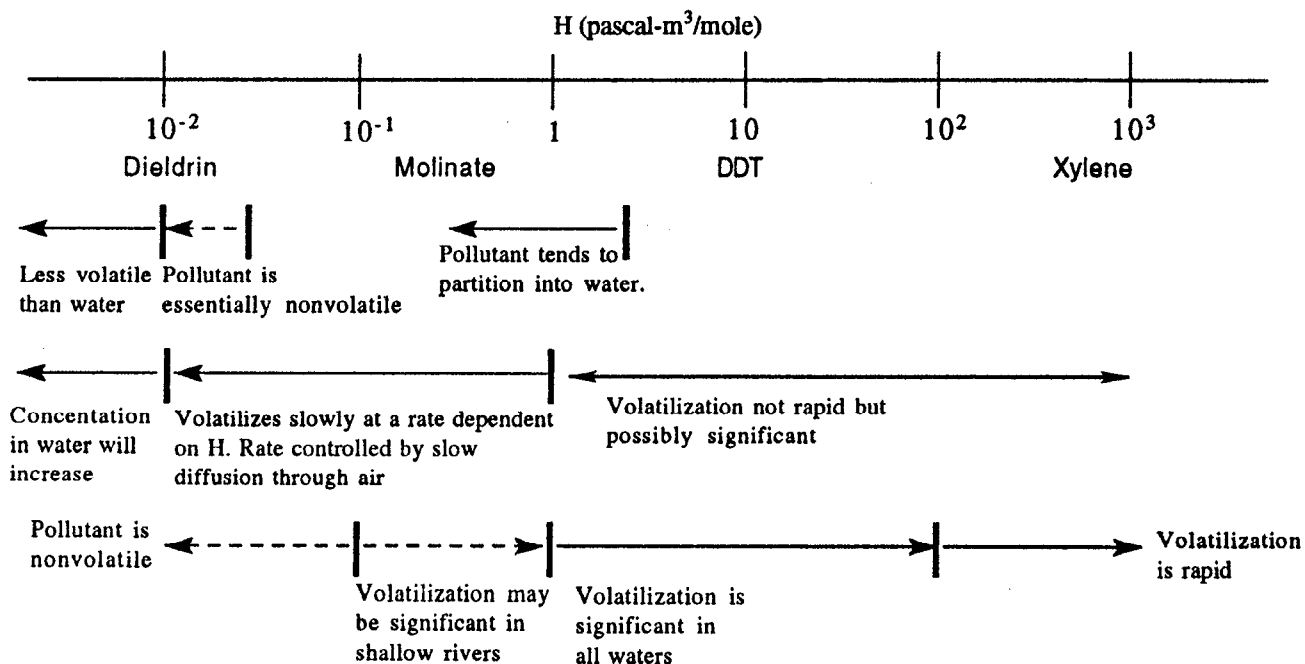
Chemical	Structure	H (Pa·m ³ /mol)
Atrazine		0.00029
Parathion		0.012
Dicamba		0.027
Chlorpyrifos		1.75
DDT		2.36

Environmental Significance

Chemicals with a high HLC tend to volatilize from water and be distributed in the atmosphere. A chemical with a low HLC will tend to accumulate in water and soil, rather than volatilize. This can be an environmental concern since the accumulation of chemicals in water can have adverse effects upon living organisms.

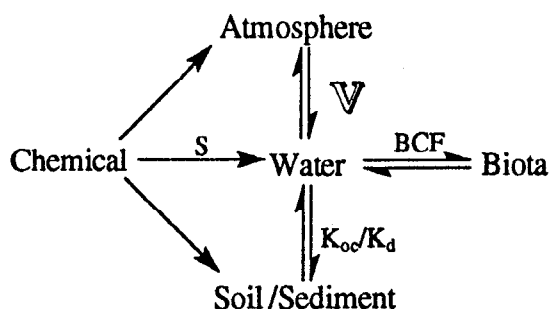
Chemicals in the air can partition (move) into water droplets in clouds and fog. If the HLC is low, substantial amounts of the volatilized chemical will dissolve in the water droplets and be transported back to the earth's surface by rain. This process of a chemical moving from the gas phase into water droplets and being deposited onto the earth's surface is called wet deposition. Dry deposition is another process that occurs when the chemical is adsorbed onto soil particles in air which is deposited on the earth's surface.

The following figure gives an overall view of HLC values and the significance that they have.



(Lyman 1990)

Chapter 8: Volatilization



Introduction

The three chapters entitled Henry's law constant, vapor pressure, and volatilization are all interrelated in that they deal with how chemicals transport from a surface into the atmosphere. To obtain a full understanding of this transportation process, all three chapters should be read.

Volatilization is one of the main transport pathways by which pesticides move from water and soil surfaces into the atmosphere. Some pesticides are more volatile than others, so they will differ in the amount that is transported. A chemical that is extremely volatile is of concern since an airborne pesticide can be quickly spread over a large area by wind. A chemical that is not volatile can accumulate on the soil or water surface and be transported down through the soil layer to ground water.

Definition

Volatilization is a process where a chemical is transported from a wet or dry surface into the atmosphere. There is no set variable that defines volatilization, however, it can be described by: flux (the amount of chemical that flows from a unit surface area into the air), or half life (how long it takes for half of the chemical to volatilize). Flux is generally expressed in $\mu\text{g}/\text{cm}^2\cdot\text{hr}$ or $\mu\text{g}/\text{cm}^2\cdot\text{sec}$, which means micrograms (μg) of chemical that volatilizes per square centimeter (cm) per hour (hr). Chemicals do not have constant volatilization rates since they greatly depend on climatic conditions (wind, temperature, etc).

A chemical can volatilize from water, and from wet or dry soil. Volatilization from these surfaces is governed by various physical, chemical, and environmental factors which means that the rates will be different for each chemical depending on the environmental conditions. Some of these factors will be discussed in the following sections.

Factors Influencing Volatilization

Wind

When a chemical volatilizes it moves into the atmosphere and away from the surface. The wind carries away previously volatilized chemical which causes more to be volatilized. As the wind speed increases so does the volatilization rate. Of the factors affecting volatilization, wind is the most important volatilization rate regulator when it is present.

Terrain/Fetch

The flow of air over soil or water is affected by objects such as trees or plants. Those objects cause air turbulence that can slow air flow over a field, which could slow down the volatilization process. Fetch is a term that is used to describe how clear a field is of obstructions.

Temperature

Temperature affects several aspects of volatilization. An increase in temperature generally increases the vapor pressure and volatilization rate. An increase in temperature will increase water and chemical evaporation rates. If all of the water evaporates off the soil, non-polar compounds will be strongly bound to the soil, so volatilization will decrease with dry soil.

Chemical properties

If the chemical is non-polar it will tend to move onto the soil and water surface. Whether the chemical will move into the gas phase at this point depends on the chemical. Some will readily volatilize and others won't. A small difference in structure can make a world of difference in volatility.

Solubility

If a chemical is not very soluble in water it will have a tendency to be pushed out of solution (like oil and water, they don't mix well). The pushing can be onto soil or the water surface. This movement onto the water surface will increase the volatilization. Chemicals that are not very soluble are non-polar chemicals (see polarity on page 4). Currents and water flow can inhibit non-soluble chemicals from reaching the surface by keeping the chemicals mixed in water. Chemicals that are polar will be very soluble in water so the volatility will generally not be high.

Soil

Soils that have a high organic content will strongly adsorb non-polar chemicals, which will decrease the amount that gets to the water surface for volatilization. K_{oc} (soil adsorption coefficient) values are generally good indicators of how a chemical will interact with soil. Polar chemicals are affected by clay content in soils, since there is a strong attraction between them. As the clay content increases, the volatilization of polar compounds decreases.

When a chemical is deep in soil, its volatility will be affected by its ability to migrate to the surface. If it is strongly bound it moves up very slowly. Weak acids are slightly polar which can make them weakly bind to non-polar organic soil. This enables these chemicals to migrate upward through soil to the water/air interface.

Molecular properties

As the molecular weight increases, the volatilization generally slows down because larger molecules move slower and they are not moving fast enough to go into the gas phase. A chemical's shape and structure also affect the volatilization rate since they can influence how strongly the chemical bonds to soil or water.

Concentration

Higher chemical concentrations will mean that more chemical is present in the water, so more will reach the surface and be volatilized.

Vapor pressure

Vapor pressure can be used to calculate Henry's Law Constant which is an indicator of the volatilization of a chemical. Pesticides will volatilize from soils differently according to the adsorbing surfaces. Vapor pressures vary from chemical to chemical depending on their structure.

Determination of Volatilization Rates

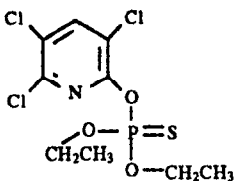
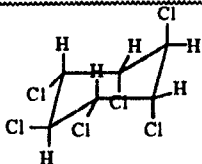
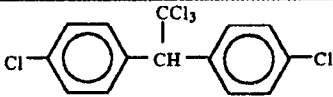
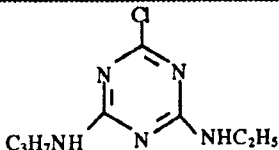
Flux is generally measured in an open field during and after application of a pesticide. The equipment is set up at different sites in the field. This equipment consists of anemometers positioned on a pole at different heights to measure the wind speed. Air samplers positioned at different heights pump air through a column filled with resin which absorbs chemicals present in air. The wind and amount of chemical found at each height is used to determine the flux (the amount of chemical that flows from a unit surface area into the air).

Estimated

The calculation of volatilization rates is not an easy one. Many factors must be taken into account. Some of these factors include: physical properties of the chemical (vapor pressure, Henry's Law, polarity, aqueous solubility, etc.), environmental conditions (i.e. wind), amount of soil and water present, ability of the chemical to move upward through soil, etc. Researchers have created models that combine these variables which enable them to calculate volatilization rates.

Comparison of Volatilization Rates

Values that represent volatility are flux and half life. No flux values will be shown in the following table because the values vary depending on temperature, wind, fetch, etc. Half life is the time it takes for 1/2 of the chemical to volatilize into the gas phase. The following table shows half lives ($t_{1/2}$) and other physical properties that are relevant to volatilization.

Chemical	Structure	Solubility mg/L	Vapor Pressure Pa	H' no units	$t_{1/2}$ hours
Clorpyrifos		1.1	2.5×10^{-3}	3.3×10^{-3}	72
Lindane		7.3	1.2×10^{-3}	2.2×10^{-5}	16.8
DDT		1.2×10^{-3}	1.3×10^{-5}	1.7×10^{-3}	1008
Methyl Bromide	CH_3Br	1.3×10^4	1.8×10^5	0.56	3.1
Atrazine		30	3.7×10^{-5}	1.1×10^{-7}	1080

(Lyman 1990)

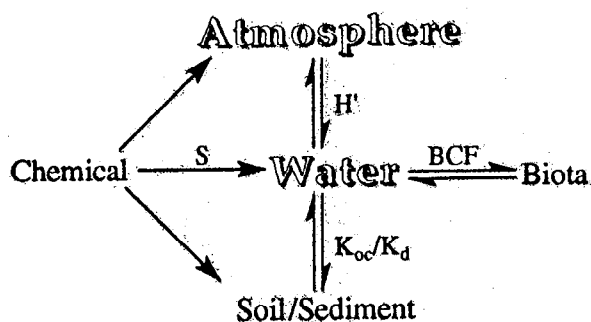
Environmental Significance

The volatilization rates of a chemical is an excellent indicator of the method of transportation by which the pesticide will be dispersed in the environment. These rates provide information about how much chemical can be present in air versus soil and water.

The following are some points to remember:

- 1) Chemical properties influence volatilization, but the rates are generally governed by wind, temperature, location, and fetch.
- 2) A non-volatile chemical that migrates and accumulates at the surface can be transported to other areas by water runoff.

Chapter 9: Photolysis

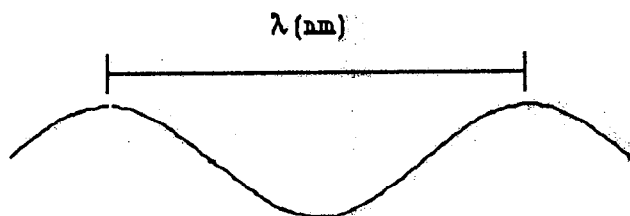


Introduction

Large quantities of pesticides are lost by volatilization into the atmosphere. In the atmosphere, there are two major degradation pathways that occur. The first is photochemical reactions caused by sunlight and the second is free radical reactions. The products formed may or may not be more toxic than the parent chemical. Photochemical reactions can take place in air or water when sunlight is present.

Definition

Light from the sun can be defined as bundles of energy called photons which move in a wave-like manner. The sun emits waves of many different wavelengths (λ = measure of the difference in length between the crests in a wave). The following illustration shows a wave with its wavelength (λ) in nanometers.



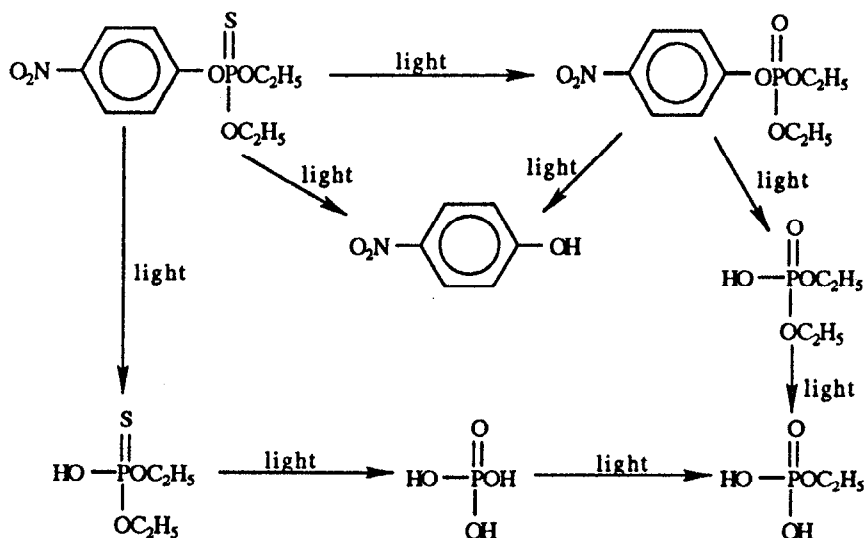
Molecules can absorb waves as energy, which can cause chemical bonds to be broken. The wavelengths of concern for pesticide degradation are between 290-400 nm, which comprises about 4% of the wavelengths emitted from the sun. Wavelengths <290 nm are filtered out by ozone in the atmosphere and wavelengths >400 do not have sufficient energy to break chemical bonds.

Chemicals can be degraded directly or indirectly:

- 1) A pesticide can react directly with sunlight, breaking its bonds.

2) Light can photolize (break chemical bonds) other molecules in air which can then in turn react with pesticides.

The first reaction occurs when photons from sunlight cause the breaking of a chemical's bonds. The total decomposition of a pesticide in air can take several steps which is illustrated by the following photo-decomposition of parathion.



The reaction above shows how different pathways can be followed in the photolysis process. The reaction rate for each pathway proceeds according to the surrounding conditions.

The second type of photolysis occurs when sunlight reacts with various molecules present in air. These include: O_3 (ozone), NO_2 , OH , and O_2 . The following reaction is an example of how water reacts with sunlight to split H_2O into $\cdot\text{OH}$ and $\cdot\text{H}$.



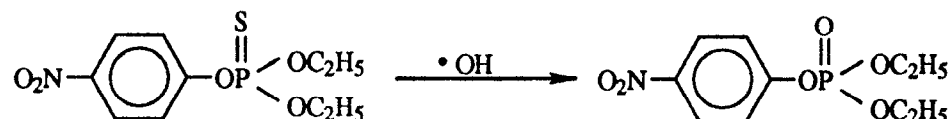
Each break down product retains one unpaired electron (this is represented by the single dot next to $\cdot\text{OH}$ and $\cdot\text{H}$). A molecule with an unpaired electron (called a free radical) is unstable and will react quickly. These free radicals can react with pesticides to form new products. Several different products can be formed. Free radicals react quickly and if enough are formed, anything nearby can be completely degraded.

A study was performed on the decomposition of organophosphorous compounds by free radicals. The results showed

the following atmospheric lifetimes of pesticides when compared to the free radicals present (Plimmer 1991).

$\cdot\text{OH}$	$\cdot\text{NO}_3$	$\cdot\text{O}_3$
0.8 hr to 2.1 days	2.9 hr to >48 days	>42 days to >275 days

Hydroxy radicals ($\cdot\text{OH}$) are the primary radicals that degrade chemicals in the atmosphere and water. The following is a hydroxy radical reaction with parathion to form paraoxon.



Radicals can be formed from either pesticides or other molecules. When a radical reacts it generates another radical. This process continues generating radicals which can degrade whatever is in their path.

Factors Influencing Value

Time of day

The rate determining step in photolysis is the amount of photons present that can react with the molecules. At midday, the sun is at its apex and light has to travel through the least amount of atmosphere to reach the ground. This means that less photons will be filtered out by ozone causing more photochemical reactions to occur. In early morning and evening the sun is at an angle so light must travel through more of the atmosphere causing more photons to be filtered out.

Photochemical degradation processes increase with temperature, so the maximum degradation rates will occur at midday.

Weather

Clouds can prevent light from reacting with molecules to form radicals, which will slow down the degradation process

Radicals Present

The amount of ozone and other free radicals present can greatly influence the rates. Increases in free radical concentration can speed up the degradation process.

Particulates

Some chemicals are not degraded by light because the wavelength needed is not present. When a molecule is absorbed onto a solid particle in air, the binding of the molecule onto the surface can change the bond strengths within the molecule. This can affect the

absorbance wavelength needed for degradation. The pesticide might now be degraded by light.

Particulates can have a negative affect upon photolysis. The particles in air can scatter light, preventing photons from reaching molecules. This will decrease the amount of radicals formed and the amount of pesticide that is degraded by light directly.

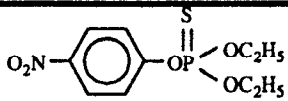
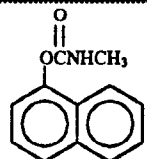
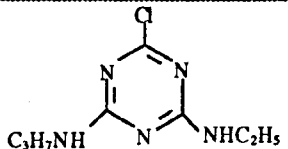
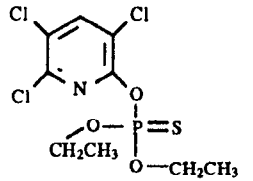
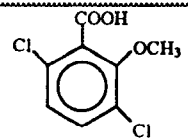
Water Depth

Photochemical reactions decrease with water depth due to a decrease in the amount of light present.

Determination of the Rate of Photochemical reactions

The rate of photochemical reactions in water and air is very difficult to determine because it is strongly influenced by environmental factors. These rates can be determined by combining the reaction rates of direct photodegradation, free radical reactions, and environmental conditions. Rates are measured under ideal conditions in the laboratory. The rate of degradation is usually expressed $t_{1/2}$ (half life).

Value Comparison

Chemical	Structure	$t_{1/2}$ Air	$t_{1/2}$ Water
Parathion		5 minutes in air	10 days
Carbaryl		12.60 minutes with $\cdot\text{OH}$ radical	6.6 days
Atrazine		2.6 hours with $\cdot\text{OH}$ radical	25 hours
Chlorpyrifos		6.34 hours with $\cdot\text{OH}$ radical <i>won't react with ozone</i>	22 days
Dicamba		2.42 days with $\cdot\text{OH}$ radical	6 days

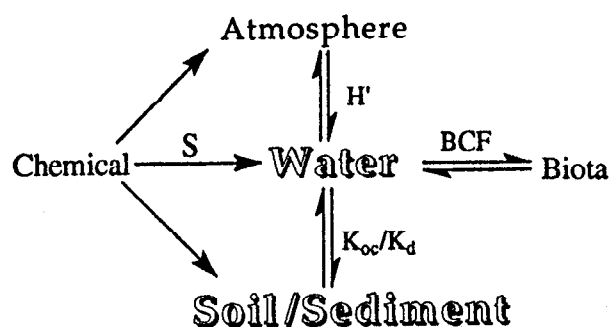
(Howard 1991)

Environmental Significance

Photochemical and free radical reactions are major degradation pathways in the atmosphere, so an understanding of the products that are formed is important. The products formed by photolysis may or may not be more toxic than the parent compound. Once a pesticide has been degraded, a major removal process for chemicals is to precipitate out of air and return to the earth's surface. Another removal process is for the products to be dissolved in rain and fall back to earth.

The most important factor in determining the rate of photolysis is the amount of light (photons) present.

Chapter 10: Microbial Metabolism

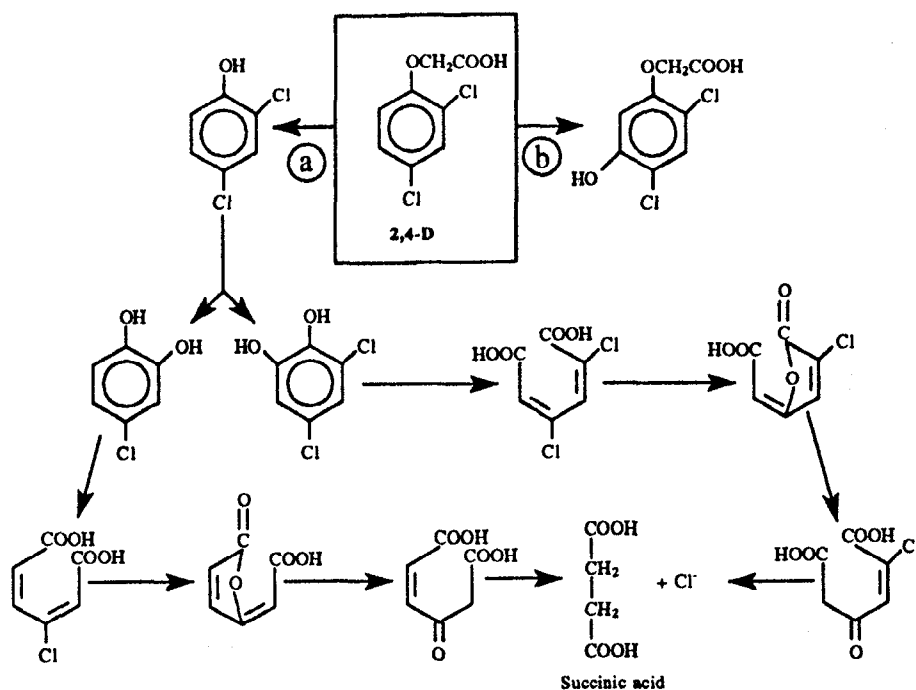


Introduction

Microbial metabolism of pesticides is an important degradation process in water and soil. The process can take several steps and the end goal is to mineralize the chemical. Mineralization is the process of changing a chemical into the basic components of CO₂, H₂O, and mineral salts. Higher organisms, such as fish, are able to metabolize chemicals but they are not able to mineralize them. There are four types of microbes: bacteria, fungi, protozoa, and algae. Bacteria and fungi are the most abundant in nature so they are the most important in biological transformation processes.

Definition

Microbial metabolism is a process by which a chemical is absorbed into the cell membrane of the microbe. Enzymes within the microbe break down the chemical into smaller fragments. Many microbes live off the energy released from the breaking of these chemical bonds. In an ideal situation, the end products of the metabolism process are minerals. Oftentimes, the enzymes present are unable to completely degrade the chemical. The products that are formed may or may not be more toxic than the parent chemical. These products could accumulate in the microbe and kill it, or the chemical could be released back into the soil so that some other microbe might be able to complete the degradation. The metabolism process is generally a several step process. The following figure shows the microbial degradation of 2,4-D, which is called the phenoxy alkanoic acid pathway. The degradation process can follow different pathways depending on the microbes present. Path 'a' occurs when the bacteria *Flavobacterina* and *Arthrobacter sp* are present. The second path 'b' occurs when the fungus *Aspergillus Niger* is present.

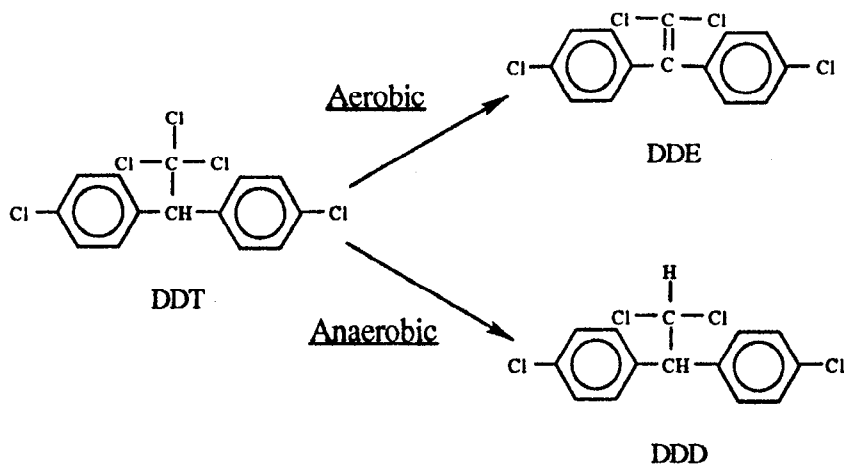


The half life of the preceding degradation of 2,4-D is generally one week.

Microbe distributions are not homogeneous in soil. There are different populations of microbes which are close to the surface. This is due to the fact that microbes naturally live off material excreted from a plant's roots. Pesticides are generally degraded by microbes along with material excreted by the roots of plants.

Bacteria account for 65% of the total bio-mass in soil, so they generally account for most degradation processes. Bacteria dominate the degradation process in alkaline soils and water ($\text{pH} > 5.5$). Fungi dominate the degradation process in acidic soils.

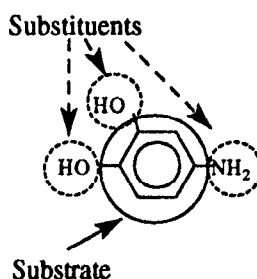
The surrounding conditions will determine whether aerobic or anaerobic metabolism will occur in the degradation of a pesticide. Aerobic metabolism is a process where oxygen is utilized to oxidize a chemical. The second is anaerobic metabolism, a process where oxygen is not present, so degradation occurs via some other pathway. Aerobic metabolism generally occurs in soil but not as much in water because less oxygen is available for use in water. In soils, the first layer degrades chemicals via aerobic metabolism because air (O_2) flows over the surface. Below this layer, anaerobic metabolism occurs because of the lack of oxygen. The following illustration shows an example of each process.



How Microbes Work

Reactions

In a microbial environment there are four categories of reactions: reduction, oxidation, hydrolysis, and conjugation. Substituents on the pesticides substrate are changed by enzymes. The following diagram shows the difference between a substituent and substrate

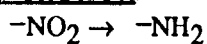


The following table shows examples of possible degradation reactions.

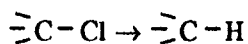
Reduction

Nitro

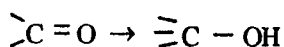
Reaction



Aliphatic Cl

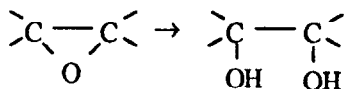


Cabonyl

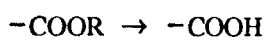


Hydrolysis

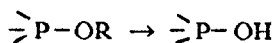
Epoxide



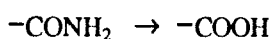
Carboxylic ester



Phosphate ester

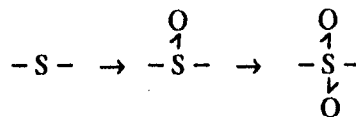


Amide



Oxidation

Sulfoxidation



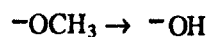
Desulfuration



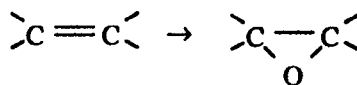
N-dealkylation



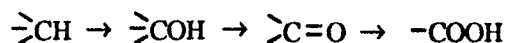
O-dealkylation



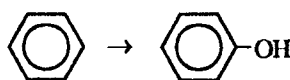
Epoxidation



C-hydroxylation

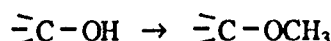


Benzene ring
hydroxylation



Conjugation

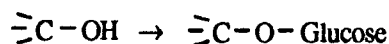
methylation(fungi)



Acetylation(bacteria)



Glucosylation
(bacteria)



Factors Influencing Value

Water Depth

Different microbes exist at different water depths. A chemical may or may not be metabolized depending on the microbes present at that depth. Also, at different depths the temperature is different, so at lower depths the rate of metabolism will be slower because of the lower temperature.

Mobility

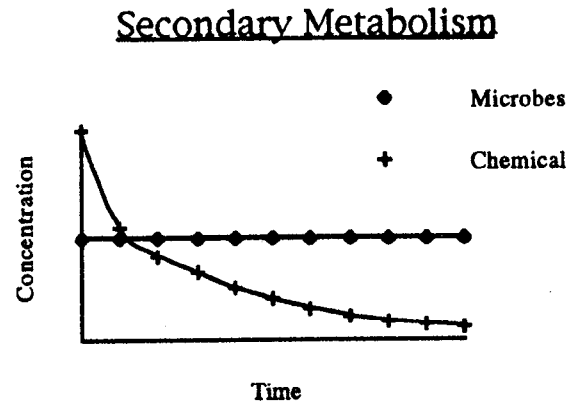
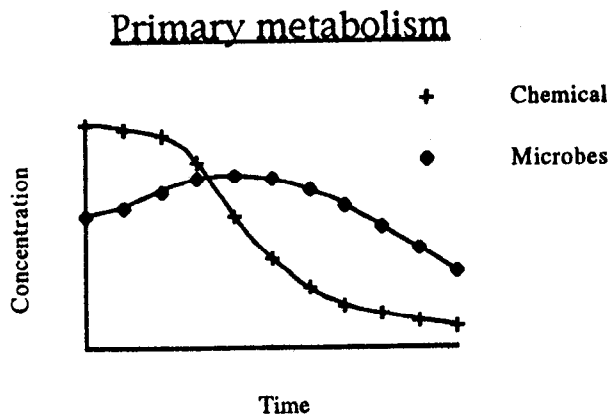
For biodegradation, a chemical needs to be absorbed through a microbes' membrane so that the enzymes can do their work. If a chemical is strongly bound to soil the biodegradation process cannot occur. DDT is an excellent example of being so strongly bound by soil that it can't be degraded by microbes. The organic content in soil strongly influences the binding of non-polar chemicals in soil (see Soil Adsorption Coefficient on page 19).

Most microbes move more freely in water than in soil so chemicals in water will be degraded faster in water than in soil.

Primary/Secondary Metabolism

Primary metabolism occurs when microbes are able to derive energy to live from the metabolism of a chemical. When a chemical is applied to soil the microbe population increases because it is food for

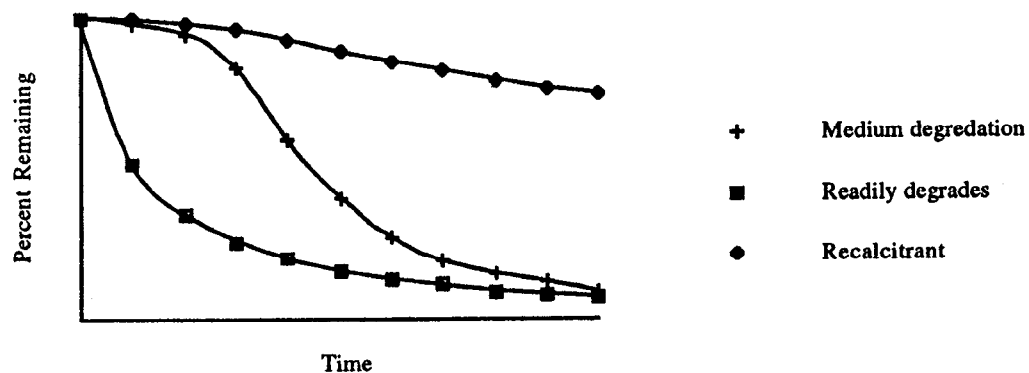
the microbes. When the chemical is depleted, the microbial population decreases. The following graph labeled primary metabolism shows this point.



The second graph shows that for secondary metabolism, the microbe population is not dependent on the chemical concentration. This is because microbes do not use the chemical for energy to live. The chemical is degraded by the microbe while it degrades other material in the soil (co-metabolism).

Pesticide

The rate at which a pesticide will degrade depends on the reactivity of the substituents bonded to the substrate. Some react faster than others. Some pesticides will be recalcitrant (persist in the environment), degrade immediately, or persist for a short term until the microbe population increases enough to completely degrade the pesticide. The following graph shows how much of these three types of pesticides degrade over time.



Concentration

If the concentration of the chemical is too low, the microbe population might not increase causing degradation to be slow. If a chemical's concentration is too large the process can be slowed because

the oxygen is depleted quickly, and oxygen may not be replenished at a fast enough rate.

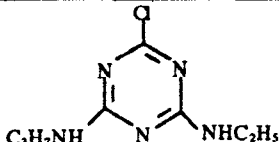
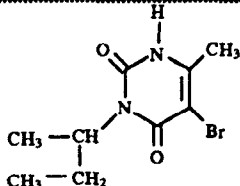
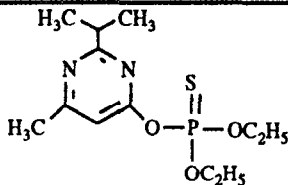
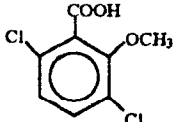
Conditions

The rate of metabolism is also influenced by pH, soil moisture, amount of oxygen present, temperature, and salinity.

Determination of Microbial Metabolism

The rates of metabolism are impossible to determine accurately because of all the variables in the environment. Experiments are performed under controlled conditions where one takes a sample of soil or water, adds the chemical and then measures the rate of disappearance of the parent chemical.

Value Comparison

Chemical	Structure	Reaction Type	Soil	Organic Matter %	pH	t _{1/2} days
Atrazine		aerobic	loam	1.4	7.6	146
		anaerobic	loam	1.4	7.6	159
Bromacil		aerobic	silty loam	2.8	6.4	458
		anaerobic	sandy loam	2.0	7.1	198
Diazinon		aerobic	sandy loam	1.3	7.8	39.7
		anaerobic	sandy loam	1.3	7.8	15.6
Methyl Bromide	CH ₃ Br	aerobic	sandy clay loam	0.26	7.3	1.46
		anaerobic	sandy loam	0.34	7.0	1.63
Dicamba		aerobic	loam	3.8	6.1	15.3
		anaerobic	loam	3.8	6.1	88

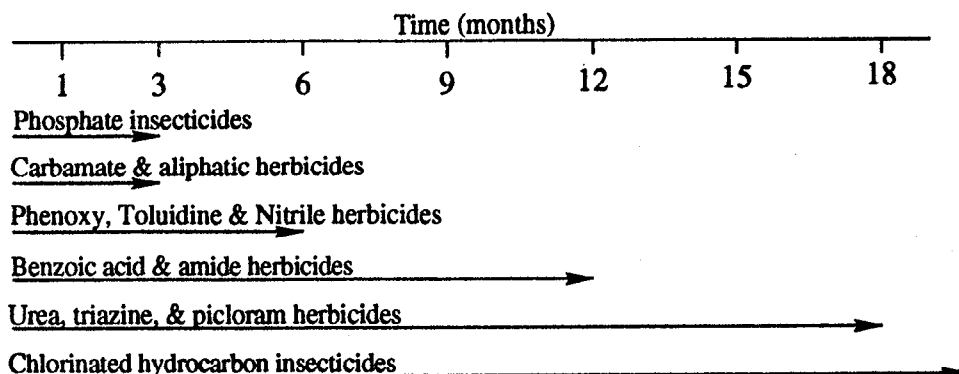
(EPA Sun Database)

The preceding values in the tables are not constant since half lives vary from soil to soil because of differences in organic content, pH, soil moisture, oxygen present, etc.

Environmental Significance

Biodegradation is not the only degradation process in soil, but it is the main one. Nature provides enzymes to degrade natural products, so pesticides that look like natural products are more likely to be degraded since enzymes will have the correct active sites. A pesticide that is unable to be degraded by microbes is likely to accumulate in soils and contaminate ground water.

Persistence in soils of several classes of insecticides and herbicides

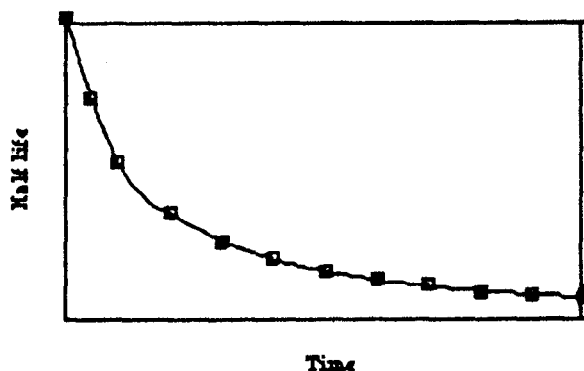


Appendix: Half Lives - $t_{1/2}$

Half life ($t_{1/2}$) is defined as the time it takes for an amount of a compound to be reduced by half through degradation or movement off site. Half lives are often used to indicate the stability of a chemical in the environment. Half life values are used to describe volatilization, hydrolysis, soil degradation, photolysis.

Half life values are influenced by a chemical's physical properties and the environmental conditions. For example, a pesticide will tend to volatilize faster in the summer than in the winter because it is warmer. These differences in conditions causes the disappearance of a chemical to vary from time to time. Half life values are the average disappearance over time.

Another factor influencing half lives are the chemical's concentration. When the concentration is high, the disappearance rate is generally faster than when the concentration is lower. This is illustrated by the half life of DDT in surface waters. If the half life is measured over 7 days the half life is determined to be 168 hours. If the half life is measured over a period of 350 days, the half life is found to be 8400 hours (Howard et. al. 1991). This shows that the half life for a chemical in the beginning is shorter than the half life of the chemical at the end. The following graph illustrates the point that half lives generally decrease over time.



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